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Hybrid organic-inorganic silica-based coatings deposited by spray technique

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Abstract

AISI 316L stainless steel is mainly used in biomedical applications, even though it suffers localized corrosion. Its protection can be achieved creating a barrier for ions migration. This paper presents the synthesis and deposition of sol gel coatings over AISI 316L, done by spray and dip-coating method, using tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and colloidal silica nanoparticles as precursors. Both coatings are analysed by optical microscopy, mechanical profilometry and electrochemical tests in simulated body fluid solution. The spray deposition technique is presented as a versatile way to generate thin layers enabling to coat complex geometries and being promising for industrial purposes.

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Keywords: Thin films; sol gel coatings; stainless steel; spray

1. Introduction

In Latin America there are many economical reasons that hinder people access to first class materials for intracorporeal permanent implants, mostly used in developed countries. For this reason, there is a strong demand of surgical grade stainless steel. However it is important to point out that this material suffers localized corrosion in the

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physiological environment, remarking that its life in service is limited and generating extra costs in Public Health budget [Katti (2004), Milosev (2002), Doorn et al. (1998)].

The improving of material's surfaces can be achieved either by chemical, electrochemical or thermal treatment, or by applying a protective coating. This generates a new surface which will interact with the surrounding media. The organic-inorganic hybrid materials have taken the attention from academics and technological institutes due to the unusual combination of physical and chemical properties that they are capable to exhibit [Brinker (1992), Guglielmi (1988)]. The family of greatest potential for development is derived from the hydrolytic condensation products of functionalized methyltriethoxysilane pure or enriched with tetraethoxysilane (TEOS).

The best prospects for developing hybrid coatings is the sol-gel method, mainly because it has a number of advantageous features compared with other deposition techniques: good adhesion, easy application, no drying problems, low temperatures of densification, the possibility to functionalize films by adding particles and / or by presence of organic groups and simple application by techniques like dip-coating or spin coating [Durán (2004), Innocenzi (1992), Kokubo (2006)]. However, these methods are only applicable for simple geometries, restricting the use and creating technological difficulties. In this context, spray technique provides a way to improve coatings deposition, not only making it easier and able to coat complex geometries, but also being a promising technique for industrial application of the organic-inorganic thin films. The spray or pulverization technique demands the optimization of several variables like gun tip openness, sol composition, carrier (type, pressure), distance to the substrate target, etc., so it is of great importance to have tools to analyze the spray performance of the deposited substance on the target.

The aim of the present work is based in the implementation and optimization of the spray deposition technique of a hybrid organic-inorganic sol gel made coating, on surgical grade AISI 316L stainless steel. The coated material with this deposition technique is compared with conventional dip-coating deposited layers.

2. Materials and methods

2.1. Substrates

The material used as substrate for coatings deposition is AISI 316L stainless steel, with a chemical composition showed in Table 1 (Cordes SA, Argentina). The shape of the samples was $10 \times 5 \text{ cm}^2$ sheets, with a "brillant" grade of surface finishing.

Before coating, the samples were cleaned with water and soap and washed with isopropyl alcohol in an ultrasonic bath for improving the coating adherence.

Table 1. Chemical composition of the used AISI 316L substrates. Values showed in % w/w.

| C | Mn | Si | Cr | Ni | Mo | P | S | N | Fe |
|------|----|------|----|----|----|-------|-------|------|---------|
| 0.03 | 2 | 0.75 | 18 | 14 | 3 | 0.045 | 0.030 | 0.10 | Balance |

2.2. Synthesis of the sol and dip-coating deposition

A sol-gel method was used to create the solution. The synthesis of the sols was done starting with the alcoxide precursors tetraethoxysilane (TEOS, Aldrich 99%) and methyl-triethoxysilane (MTES, Aldric 98%) in acidic catalysis. The stoichiometric water required for the reaction was provided by the addition of an aqueous solution of colloidal silica (40% w/w Levasil 200[®]). Ethanol was used as solvent. The TEOS/MTES relationship was 40/60 in mol and the final silica concentration for the sol was 3.33 mol/L (or 200 g/L).

The dip-coating layers were applied on the cleaned and dried substrates with a mechanical arm connected with a PLC interface (FESTO, Argentina). The process was done as it is showed in Fig. 1, where the extraction rate used is the controlling stage in the deposition process. In this case it was 20 cm/min.

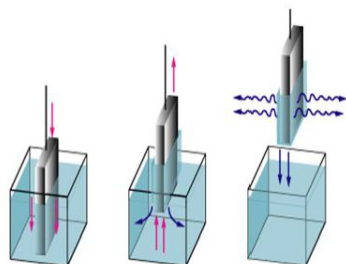


Fig. 1. Scheme of the dip-coating deposition technique

2.3. Spray deposition

An airbrush-spray gun was connected with the mechanic arm and the PLC system. The carrier used for the sol deposition was comprised air with a high efficiency filter.

The software allows to do lateral movements at controlled speed, and successively lines moving up and down. So it allows covering all the x-y 2dimmensional space. It was used a “gravity spray gun”, where the liquid to be blown is placed in a cup next to the gun and falls by gravity, Fig. 2.

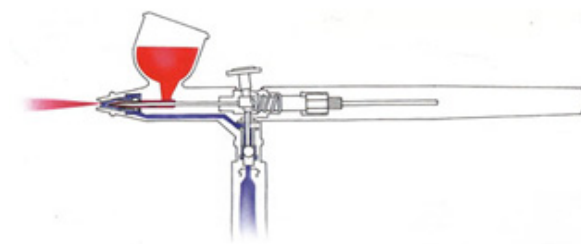


Fig. 2. Scheme of airbrush-spray gun system

After several trials and tests, the final deposition variables selected were 1 bar of pressure in the compressed air line, 13 cm distance between the extreme of the gun and the target, 250 mm/s of speed of the gun in the lateral movement (x axis), and 12 mm distance between depositions in the y axis.

2.4. Thermal treatment

After the application of the different type of coatings (spray or dip coating), a thermal treatment was done. First the layers were dried at 60 °C in oven in air atmosphere, and then treated for 30 minutes at 400 °C in the same atmosphere, with a heating and cooling rate of 5 °C/min. The aim of this treatment is to evaporate the remaining solvent and to produce densification of the layer obtained.

2.5. Coatings characterization

To analyze the wettability of the substrate with the sol, the contact angle was evaluated after different protocols of surface cleaning. Angle measurements were done with a goniometer (Ramé Hart model 500 Advanced Contact Angle Goniometer with DROP image Advanced Software). The measurement was done placing a drop of the TEOS-MTES-SiO₂ sol over the stainless steel surface, with different cleaning protocols performed to the AISI 316L sheets. The first cleaning protocol analyzed was cleaning the samples with water and soap and drying them with air gun, and the second one, cleaning them with isopropyl alcohol in an ultrasound bath and then air gun dried.

A mechanic deep profiler (KLA Tencor mod Alpha-Step D-100) was employed to measure the thickness of the coatings obtained by dipping and spray coating. For this test was necessary to performed a scratch with a diamond pencil before the thermal treatment

In order to analyze the integrity of the coatings exposed to an aggressive media, electrochemical essays were carried on. The solution used for these measurements is Simulated Body Fluid (SBF). This solution contains all the inorganic ions present in the human plasma (Table 2) [Kokubo (2006)]. The final pH of the solution was adjusted with HCl to 7.30 ± 0.05 .

Table 2. Concentration of the Simulate Body Fluid solution in mM.

| | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | Cl ⁻ | HCO ₃ ²⁻ | HPO ₄ ²⁻ |
|---------------------|-----------------|----------------|------------------|------------------|-----------------|--------------------------------|--------------------------------|
| SBF | 142.0 | 5.0 | 1.5 | 2.5 | 148.8 | 4.2 | 1.0 |
| Human Plasma | 142.0 | 5.0 | 1.5 | 2.5 | 103.0 | 27.0 | 1.0 |

Electrochemical assays were carried out in a GAMRY Ref 600 electrochemical unit (Gamry, USA) with a conventional three electrode cell. The reference electrode was a saturated calomel electrode (SCE, Radiometer Copenhagen), a platinum wire as a counter electrode and the stainless steel, either bare or coated as working electrode.

Potentiodynamic polarization curves were conducted from the corrosion potential (E_{corr}) to 1.2V and backwards, or up to a maximum current density of 0.001 A.cm^{-2} , at a sweep rate of 0.002 V. s^{-1} .

Electrochemical impedance spectroscopy (EIS) tests were registered at the E_{corr} with an amplitude of 0.005V rms sweeping frequencies from 20000 to 0.02 Hz. Impedance data fitting was performed using Zplot software [Zplot for Windows (1998)].

3. Results and discussion

The wettability of the substrate is a necessary property to ensure the perfect coating coverage. Without the cleaning with isopropyl alcohol in ultrasound bath, a drop is formed when reaching the surface with an initial contact angle of 20°, which tends to decrease in time to an almost complete wetting. When the ultrasound bath is used, the substrate reaches complete wettability at the instant the drop reaches the surface. Identical tests were done to the stainless steel surface with a surface finish made with 600 grit emery paper (to be compared with the “brilliant” surface finish). The results of the contact angles were bigger than the values obtained with the polish “brilliant” surface (around 40°). The time needed for complete wetting was three times the needed for the brilliant surfaces.

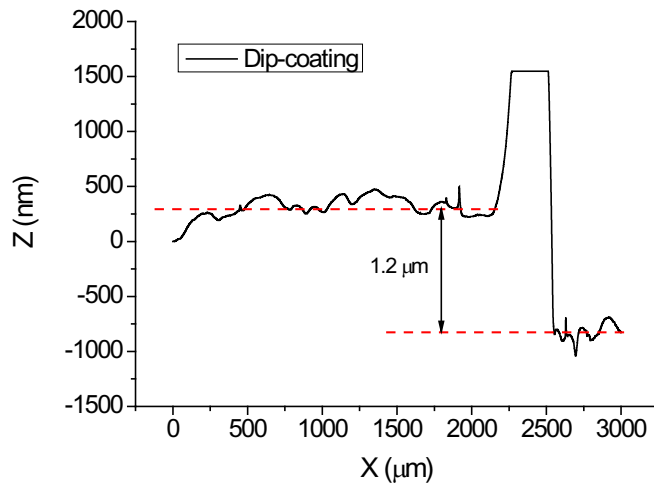


Fig. 3. Thickness of a single dip-coated layer of TEOS-MTES-SiO₂ sol on stainless steel substrate.

Figure 3 shows the profile and the thickness measured of samples done by dip coating technique, while in Fig. 4 it is shown the step made on the surface for measuring the coating thickness for the spray technique samples. When comparing thicknesses, it can be noticed that the coating made by spray technique presents a value two times higher than the one reached for dip-coating. It can also be observed material accumulation in the zone near the step, related with the plastic deformation due to the scratch. Coatings roughness can be estimated with the profiles shown in Fig. 3 and 4, where it can be seen that dip-coated samples results smoother. This feature might help to improve biological adhesion of different species, depending on the use of the coated material. In the case of an implant, the roughness could help to osteoblast adhesion and proliferation [Martin et al. (1995)].

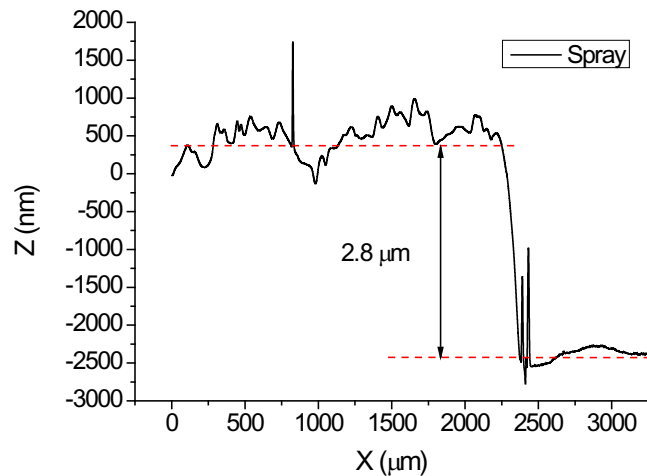


Fig. 4. Thickness of a single spray made layer of TEOS-MTES-SiO₂ sol on stainless steel substrate.

Accelerated electrochemical degradation essays were carried out in order to evaluate the response of the coated materials to a simulated biological environment.

Fig. 5 shows the behavior of the different systems under study including the bare material, by applying a raising potential from E_{corr} and measuring the current density. The samples presented very low current density values, three decades lower than the bare steel, after immediate immersion in simulated body fluid solution. The decrease in current density when compared with the bare alloy can be attributed to an area effect, since the coating serves as a barrier for the diffusion of water, oxygen and ions from the solution to the substrate. Also it is worth noticing that the dip-coated and sprayed coating systems have a wide range of pseudo passivity, making the materials in a stable state up to 0.8-0.9V when the system localized corrodes.

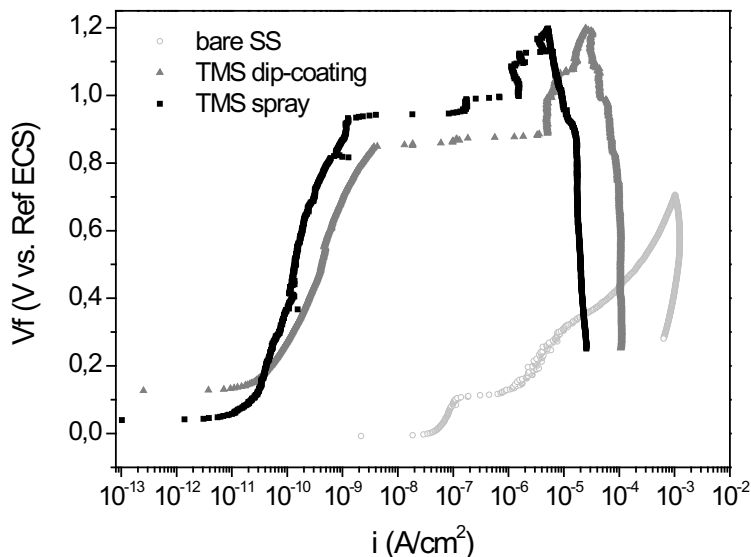


Fig. 5. Polarization curves of the coated systems: TEOS-MTES-SiO₂ sol gel film by dip-coating or spray deposition technique, immersed in SBF. The bare material is also shown.

Fig. 6 shows EIS results for the coated system in SBF in comparison with the bare alloy. The substrate shows the presence of two time constants in the phase angle vs. frequency plot related to the presence of an oxide onto the surface at high frequencies and to corrosion processes taking place in the alloy at low frequencies. Coated samples show an angle near to 90° in almost all the domain of frequencies studied, suggesting a non ideal dielectric capacitive behavior with some grade of porosity as evidenced in the decrease of the angle in the low frequency region [Carmezim et al. (2005)]. Both coated materials (either by dip-coating or spray) present an impedance modulus value (extrapolating to zero frequency) that takes into account all resistances that consider charge transfer (Fig. 6a). The total impedance modulus of the coated systems is between 3 and 4 orders of magnitude higher compared with the bare metal indicating the barrier effect of the silica based hybrid coating.

Electrochemical assays show that, although coating obtained by spray are thicker than the ones obtained by dip-coating and then the barrier effect would be expected to be greater, the formers are probably more porous, and the income of the electrolyte into the pores could be favoured when increasing the immersion time. However, since the spray technique is more versatile than dip-coating, the corrosion resistance achieved for both is competitive in this stage.

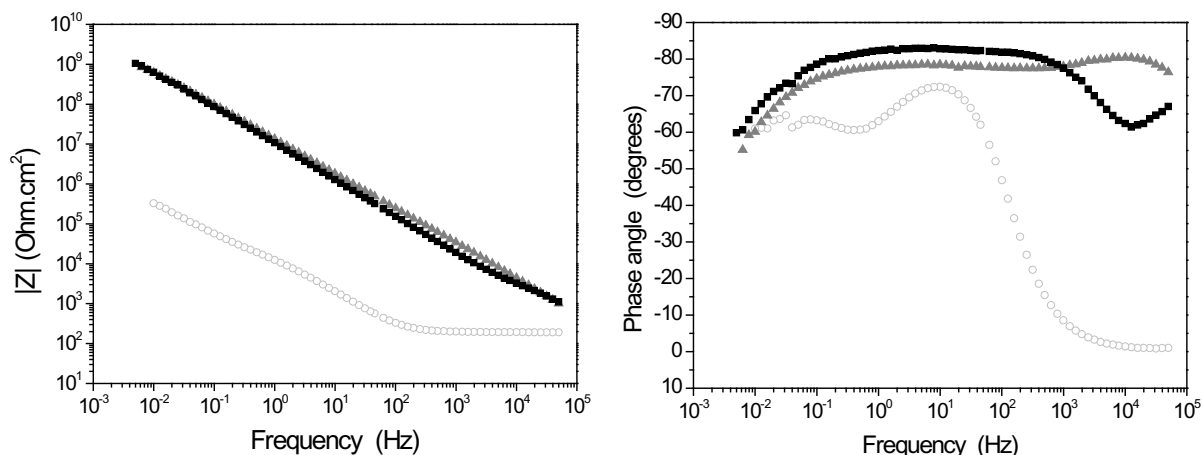


Fig. 6. (a) Bode representation of the dip coated and the spray coated stainless steel samples immersed in SBF; (a) $|Z|$ vs. Frequency, (b) Phase angle vs. frequency. \circ Bare 316L Stainless steel, \triangle TEOS-MTES-SiO₂ dip-coating system, \blacksquare TEOS-MTES-SiO₂ spray system.

4. Conclusions

Hybrid organic-inorganic silica based coatings created by sol gel method and deposited on 316L stainless steel by different techniques were analyzed. The spray deposition technique is presented as a versatile way to generate thin layers on metallic substrates, with a potential capacity of being used in complex geometries at industrial scale. The homogeneity and integrity of the traditional dip-coated thin films is also reached by the spray technique, although the roughness and inner porosity is thought to slightly affect the corrosion behavior after prolonged immersion in aggressive media.

Acknowledgements

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